

Coatings Formed on Steel by Cathodic Protection and Their Evaluation by Polarization Measurements

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Three steel specimens were continuously exposed in the laboratory for almost 5 years in city water to which was added 3 percent by weight of sodium chloride. Two of these specimens were under continuous cathodic protection, one by current from a zinc anode, and the other by current from a rectifier through a carbon anode. The third specimen was left to corrode freely.

As a result of the cathodic protection, carbonates and silicates formed protective coatings which eventually reduced the current density required for protection from about 5 to 0.02 ma/ft². A coated specimen, after being without protective current for 32 days (including 12 days out of the salt water), required only 0.3 ma/ft² for initial protection.

The instantaneous corrosion rates on the coated specimens (scratched and unscratched) while without protective currents were measured by changes-in-slope (breaks) in polarization curves. The currents at which breaks occurred in the cathodic curves were found to be related to $\Delta V/\Delta I$ values from the curves which values in turn bore a relation to the corrosion rates as measured by weight loss.

1. Introduction

When cathodic protection is mentioned in conjunction with coatings for protecting steel structures against corrosion, the coatings referred to are invariably organic in nature. Relatively little is said of the benefits of the inorganic or natural coatings such as carbonates or silicates which can be deposited as a result of cathodic protection and which the authors have found to be quite corrosion-resistant in a salt water environment. Although the protective character of such coatings, not necessarily in connection with cathodic protection, has been emphasized by other investigators it is believed that the present discussion will be of additional value and interest because the very nature of cathodic protection when properly applied is such as to automatically keep these coatings in a state of repair.

Speller [1]¹ states that silicious and carbonaceous coatings are sometimes formed on metal surfaces by adsorption in the atmosphere, underwater, and in soils, and often act as the main natural agency opposing corrosion.

Evans [2] in talking about the behavior of zinc-coated steel continually immersed in water has suggested that the carbonate electrochemically deposited on the steel, when the zinc goes into solution, may persist even after all the zinc has disappeared.

In some of the early NBS soil corrosion tests, Logan [3] attributed the protective effect of the zinc coating on galvanized pipe specimens to a protective

film found on the surface of the zinc rather than in cathodic protection by the zinc. Later, Denison and Romanoff, [4] in reporting on the behavior of galvanized steel specimens exposed to corrosive soils for 13 yr, tentatively attributed their remarkable corrosion resistance in alkaline soils to a film or coating, probably silicious in nature, that was deposited cathodically by galvanic action between the remaining zinc coating and the alloy layer on the underlying steel. The protection of the steel was obvious even though the outer zinc coating had been virtually removed by corrosion.

Hoar [5] in a private communication suggested that the protection produced by the cathodic deposition of calcium carbonate on a metal surface can persist in many cases long after the cathodic current is stopped.

Pearson [6] associates the useful ampere-hour effect of cathodic protection on ferrous materials underground with a film formed by the precipitation of insoluble carbonates. He describes the "film" formed as being effective even when barely visible and building up with time.

This paper describes the effects observed by cathodically protecting cold-rolled steel rods exposed to city water to which was added 3 percent by weight of sodium chloride. It is shown how the effectiveness of the coatings formed on the steel surfaces can be evaluated by the means of polarization measurements. The applied currents associated with changes-in-slope of the current-potential curve during cathodic polarization are shown to be related to the corrosion caused by physically disturbing the uniformity of a coating. The study extended over a period of almost 5 yr.

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¹ Figures in brackets indicate the literature references at the end of this paper.

2. Experimental Procedure

The experiments to be described started out as a simple demonstration of cathodic protection for students spending their vacations working on various projects at NBS. A $\frac{1}{2}$ -in. diam rod of cold-rolled steel was coupled to a zinc rod through a milliammeter and exposed to Washington City water to which had been added 3 percent by weight of sodium chloride. The steel rod was protected by tape at the water line and had approximately 0.1 ft² of surface (9 in. of its length) exposed to about 17 liters of the salt water contained in an open Pyrex jar. Henceforth, all currents will be expressed as apparent current densities in ma/ft² or ma/dm². During initial exposure, the galvanic current rapidly diminished from 200 ma/ft² to 10 ma/ft² and after 3 weeks of exposure was down to 6.0 ma/ft² at which time the rod was removed from the water, washed under running water, and examined. A white chalklike coating which could readily be scratched off was noticeable on the lower end of the rod. The rod was put back into the water and again coupled to the zinc. As time went on, the galvanic current became smaller until, after 1 yr of exposure, it was 0.5 ma/ft². During the exposure period it was observed that the potential of the steel, with reference to a saturated calomel half cell (used throughout this investigation), was about -1.0 v when read immediately after breaking the galvanic circuit. After the circuit had been broken for 1 min, the potential of the steel was still between -0.85 and -1.0 v. At the end of the year, the rod was uniformly covered with the chalky deposit (2 to 3 mils thick) containing zinc silicate as shown by the X-ray diffraction powder pattern analyses. Figure 1 is a photograph of the rod showing the white coating. On this occasion, no rust was in evidence, anywhere, even under the tape laps.

Upon the conclusion of the foregoing experiment 3 additional weighed steel specimens, prepared as the one previously described, were individually exposed in 3 Pyrex jars each containing 17 liters of city water to which had been added 3 percent by weight of sodium chloride. One specimen, No. 1, was left to corrode freely and act as a control. Specimen No. 2 was connected galvanically to zinc and specimen No. 3 received protective current from a $\frac{1}{2}$ -in. diam carbon rod fed by a copper oxide rectifier. Here again, the specimens were set up primarily for demonstration purposes, but protective currents were measured from time to time as were the potentials of specimens Nos. 2 and 3 under cathodic protection. The water level in the open jars was never permitted to drop below the tape line, makeup city water being added weekly to compensate for evaporation loss.

After 12 months the 3 specimens were removed from the jars, cleaned and reweighed. The specimens were put back into the same jars and electrolyte from which they had been removed. The specimens were not removed from the electrolyte again, except for brief periods, until the 56th month and finally

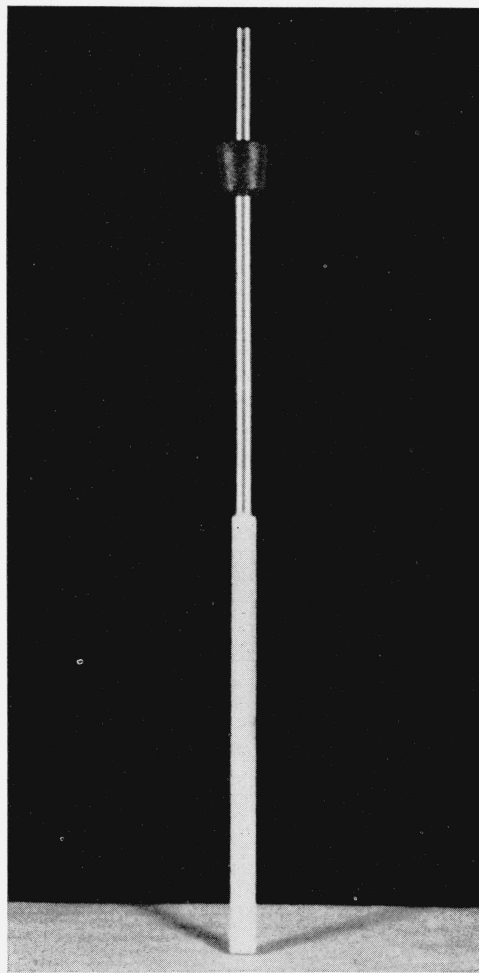


FIGURE 1. Inorganic coating formed on steel cathodically protected by zinc for one year in a 3 percent sodium chloride solution.

for chemical analysis of the coatings formed on the specimens under cathodic protection, and for cleaning and reweighing after 57 months of exposure.

Until the 55th month, specimens Nos. 2 and 3 were continually under cathodic protection except for relatively brief periods which will be discussed later. The potential of specimen No. 2 (connected to the zinc) was always well within the protective range because of the good conductivity of the electrolyte, while the potential of specimen No. 3 was always at least at -0.77 v and usually more electronegative. After 34 months exposure, a potentiometer was shunted across the secondary of the rectifier supplying specimen No. 3 and the applied voltage adjusted to a value consistent with maintaining a minimum protective potential of approximately -0.77 v. By this time, a uniform natural coating was in evidence on specimen No. 3 and it was found on further reductions in the current applied to No. 3, after 52 months, that it was easily possible to maintain a polarization potential of -0.77 v with 0.1 ma/ft². In fact, even with this low-current density the potential of specimen No. 3 was usually more electronegative than -0.77 v.

During the last 3 months of exposure cathodic polarization curves were obtained on specimens Nos. 2 and 3. Curves were also obtained on specimen No. 1 (freely corroding) before and after the removal of the heavy accumulation of corrosion products. After cleaning, curves were obtained during a 14-day exposure period to provide data on the initial corrosion rate of the unprotected rod and for comparison with the curves obtained on specimens 2 and 3.

Potential checks were made with a 200,000 ohms/v voltmeter. Polarization data were obtained with a two-pen (current and potential) strip chart electronic recorder. The polarizing current was varied by linear increments in the applied voltage which were obtained with a synchronously driven 10-turn potentiometer. The Holler null circuit described in a previous paper [7] was used in conjunction with the recorder but IR-drop compensation was unnecessary in the low-resistivity electrolyte.

3. Electrical Measurements and Observations

The more important information in this study pertains to the significance of the polarization data and the discussion later pertaining to the formation of the natural coatings and their importance in cathodic protection. Before discussing the polarization data, however, some of the prior observations on specimens Nos. 1, 2, and 3 or in order.

The potentials, currents and other observations pertaining to these specimens during the first 12 months of exposure are of interest. Until the end of the first month specimens Nos. 2 and 3 each received 5.0 ma/ft² of protective current, with the potential of No. 2 around -0.97 v and No. 3 at -0.90 v. After the first month, the protective galvanic current on specimen No. 2 rapidly diminished to 0.6 ma/ft² for at least 6 months of the year and never exceeded 1.2 ma/ft². On the other hand, the current applied to specimen No. 3 usually varied between 5 and 13 ma/ft². The potentials for specimen No. 2 varied during the year between -0.97 v and -1.0 v while the potential for specimen No. 3 varied between -0.80 v and -0.97 v, averaging about -0.85 v. All potentials were read while the anode was momentarily disconnected. During the year, the voltage applied between the carbon anode and specimen No. 3 was very close to 2 v, so it can be assumed safely that the driving voltage was greater than the driving voltage between the zinc anode and specimen No. 2, even allowing for considerable anodic polarization of the carbon anode. At the end of the year, the 3 specimens were removed for examination, cleaning and reweighing. Specimen No. 1 was cathodically cleaned in salt water at a current density of 1 amp/ft² for 3 hr and then wire-brushed by hand to the bare metal. The specimen lost 4185 mg during the first 12 months which is equivalent from Faraday's Law (assuming 100% corrosion efficiency) to an average corrosion current density of about 4.6 ma/ft². Specimens Nos. 2 and 3 were washed under hot running water and examined.

Number 2 had a fairly adherent coating, similar to that formed on the preliminary demonstration specimen exposed earlier. Although no rust was visible, the specimen was subjected to a cathodic current density of 1 amp/ft² for 1 hr. After considerable wire-brushing and reweighing, specimen No. 2 weighed 110 mg more than before exposure. The increase in weight was attributable to the coating which was still visible after the wire-brushing. Similar treatment of specimen No. 3, also without evidence of corrosion, revealed an increase in weight of only 10 mg. Before cleaning, specimen No. 3 had a dark-green appearance. Thus, during the first year, the coating formed on specimen No. 2 was apparently superior to that on specimen No. 3. This explains the lower current density required to protect specimen No. 2.

After the 3 specimens were cleaned and reweighed they were put back into their respective jars with no other changes. Currents and potentials were about the same during the next year as they had been previously. After 24 months of exposure, specimen No. 3 was taken out of the salt water for a few hours. It was brushed under hot running water with a brass-bristle brush, permitted to dry and then weighed. The coating now weighed about 25 mg and its appearance was the same as after 12 months. The specimen was put back into the salt water with cathodic protection. After 33 months of total exposure time the protective current, which was 3 ma/ft² at the time, was temporarily removed from specimen No. 3. Immediately after opening the circuit, the potential was around -1 v. After 5 min, the potential was -0.82 v and after 35 min with no protective current the potential was -0.77 v. The protective current was then restored at an arbitrarily reduced value of 1 ma/ft² which soon polarized the steel to -0.8 v. The next day the potential was -0.84 v and the current 0.5 ma/ft², a condition that persisted for the next 7 days. The applied voltage between the carbon anode and the steel specimen was further reduced to 1.45 v and it was found that for several days 0.25 ma/ft² was sufficient to hold the potential at -0.77 v. During the next 18 months the current density varied between 0.1 and 0.5 ma/ft² except for one occasion when it went to 1 ma/ft² when the power failed over a weekend. This resulted in a pinhole through the natural coating as evidenced by a spot of rust. The coating soon re-formed over this spot and the current again gradually lowered until, between the 52d and 55th months of exposure it varied between 0.1 and 0.25 ma/ft² with the potential around -1.0 v. At these relatively low-current densities no attempt was then made to reduce the current further but it was obviously possible to do so, as will be shown later, in view of the potential.

An experience with specimen No. 2 was also rather enlightening. After 42 months exposure, the zinc anode was disconnected and the potential of the specimen measured at intervals during a period of 8 hr. Prior to opening the circuit the protective current was 0.5 ma/ft². Immediately after breaking the anode circuit, the potential of the specimen was

−0.96 v and after 30 min it was −0.83 v. After 1 hr without protective current, the potential was still −0.78 v and after 6½ hr it was −0.62 v with no visible evidence of rusting. The protective current was left off over the weekend. After 64 hr the potential was −0.665 v and two small spots of rust were evident on the coated surface, otherwise there was no evidence of corrosion. The rust was brushed off and the specimen put back into the solution under protection by the zinc. Over the weekend, although no measurements were made, the potential probably rose to a value somewhat more noble than −0.62 v and then when breakdown of the points on the surface occurred, the potential gradually drifted in the more electro-negative direction. A similar potential drift in the noble direction was noted on steel specimens in soils [8] after protective currents were removed and then a reversed trend in potential drift as corrosion again commenced.

A repetition of the foregoing experiment followed by polarization measurements was conducted on specimen No. 2 after 56 months total exposure time. At this time, the galvanic current had decreased to 0.1 ma/ft² from a value of 0.5 ma/ft² on the previous occasion. Within a few sec after opening the galvanic circuit the potential of the steel was −0.92 v at which time a cathodic polarization curve was obtained. The polarization was rather rapid, $\Delta V/\Delta I$ being 1000 mv/ma from 0 to 1 ma/ft². After running the curve, the potential of the specimen which had been left on open circuit drifted to −0.77 v in 2½ hr, and after 3½ hr the potential was −0.75 v. Twenty-one hours later, the potential was −0.64 v and there was no visible evidence of corrosion. Cathodic polarization curve A, figure 2, was obtained at this time. This was the first of a series of curves taken on this specimen during the following 36 days to show how damage of the coating affected the polarization, and the effect on polarization of removing the specimen from the salt water, exposing it to the indoor atmosphere for 12 days and then putting it back into the same water again.

Curve B, figure 2, shows the polarization of specimen No. 2 after 45 hr without protective current when the first visible evidence of rust appeared about 2.5 in. below the waterline, or around 1 in. below the lower edge of the tape. Curve C, was obtained after 5 days without protective current and then the specimen was removed from the water in order to scrape off some of the coating about 3 in. below the lower edge of the tape. The coating was removed in the form of a 0.2 in. wide band encircling the rod. Curve D, obtained the next day, shows the effect of the coating removal on the polarization. Curve E, was obtained after 12 days without protective current, no additional corrosion being visible other than on the two areas just mentioned. On the 14th day without protective current, this specimen was removed from its corrosive medium and exposed to the air for 12 days with the other two specimens. Just prior to putting specimen No. 2 back into the salt water, a little dilute hydrochloric acid was placed on a small area of the coating. Gas evolution, indic-

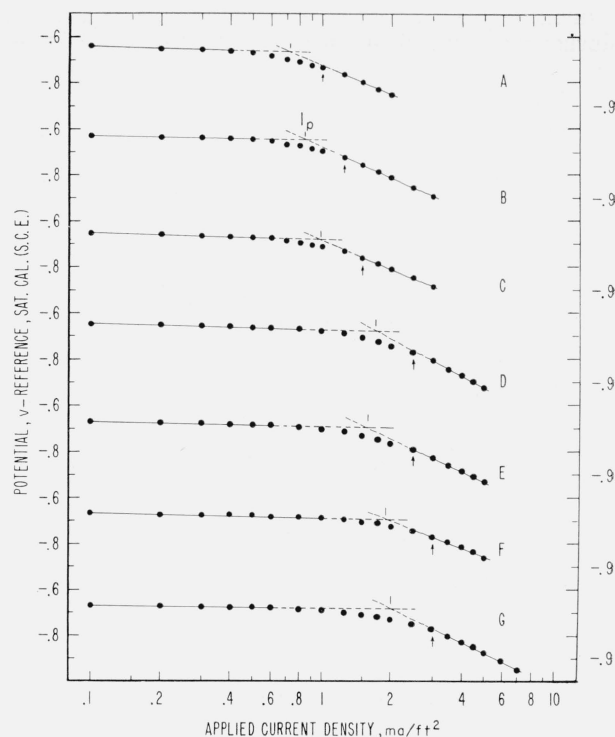


FIGURE 2. Cathodic polarization of an inorganically coated steel specimen, No. 2, in a 3 percent sodium chloride solution, as affected by progressively damaging the coating during a period of 36 days without cathodic protection.

Polarization rates $\Delta V/\Delta I$, mv/ma, through the range of applied current (density $\times 0.1$) indicated by the arrows are as follows: A, 940; B, 808; C, 707; D, 520; E, 504; F, 320 and G, 353.

ative of a carbonate coating, was observed. The specimen was then rinsed under running water and returned to the salt water from which it had been removed. The next day, curve F, figure 2, was obtained. There was some visible evidence of rust on the area touched by the acid the previous day. During the next 10 days there was no evidence of increased corrosion. On the 36th day without cathodic protection the final cathodic polarization curve, G, was obtained. After stabilization of the specimen potential, an anodic polarization curve was run. The specimen was then removed from the water for a spectrographic analysis of the natural coating formed during the 57 months of exposure and for reweighing of the specimen after removal of the coating. The anodic polarization was purposely left until the end of the experiment to avoid the possibility of disturbing the coating. The significance of the polarization curves will be discussed later.

Similar polarization studies were made on specimen No. 3 except that no attempt was made to intentionally disturb the natural coating. After 55 months exposure, the protective current on specimen No. 3 was 0.1 ma/ft² and a quick reading of its potential upon removing the current gave −1.05 v. After the circuit had remained open for 5 min, the potential was still −0.98 v. A potential-time study was then

carried out by use of the potentiometer-recorder. After 35 min without protective current, the potential was -0.97 v. Note the relatively slow decay in potential as compared with that observed in a similar experiment, previously described, after 33 months exposure. After 24, 48, 72, and 96 hr, the potentials were -0.89 v, -0.81 v, -0.81 v, and -0.76 v, respectively. The potential continued to drift in the electropositive direction until on the 9th day without protective current, the potential was -0.65 v with no visible corrosion. Cathodic polarization curves obtained on specimen No. 3 during this initial 9-day period without protective current showed that the polarization rate (designated $\Delta V/\Delta I$) was relatively high in comparison with that observed on the corroding specimen No. 1.

The protective current from the rectifier was again applied to specimen No. 3 and left on for 12 days. Within 4 hr, the potential was -0.84 v and the current density 0.3 ma/ft². After 7 days, the current density was 0.03 ma/ft², the potential -0.90 v. On the 10th day, the applied voltage from the rectifier was reduced to 1.33 v between anode and cathode. On the 12th day, the potential of the specimen was -0.85 v and the protective current density was 0.02 ma/ft². Cathodic polarization from this potential revealed $\Delta V/\Delta I$ as being 3400 mv/ma between 0 and 0.5 ma/ft² of applied current density. On the 12th day the protective current was removed and the specimen left without protection. After 24, 48, and 96 hr, the specimen potential was, -0.83 v, -0.80 v, and -0.76 v, respectively. After the second 9-day period without protection specimen No. 3 was removed from the salt water and exposed to the air in the laboratory for 12 days. This was followed by 11 additional days of exposure without protection to the same salt water from which it had been removed. Cathodic polarization curves were obtained during the two 9-day periods preceding exposure to the air and during the following 11-day period. The polarization runs were made at times when some corrosion could have been taking place, that is, when the specimen potential was electropositive to -0.77 v as shown by a previous study [9]. These cathodic curves are shown in figure 3. Curve A, was obtained on the 4th day, curve B, on the 9th day of the initial 9-day period, and curves C, D, and E during the second 9-day period preceding air exposure. Curves F and G cover the final 11-day period of exposure to the salt water. On the final day of salt water exposure, an anodic polarization curve was also obtained on specimen No. 3, after which it was removed from the salt water, washed under running water and permitted to air dry. This was followed by a spectrographic analysis of the coating, quantitative analysis for carbonates in the coating and finally, removal of the coating and reweighing.

The anodic polarization curves obtained on the final day that specimens Nos. 2 and 3 were exposed are shown in figure 4. The eventual superiority of the coating on specimen No. 3 as compared with that on specimen No. 2 is shown by the higher polarization rate of specimen No. 3. This will be discussed in more detail later in the paper.

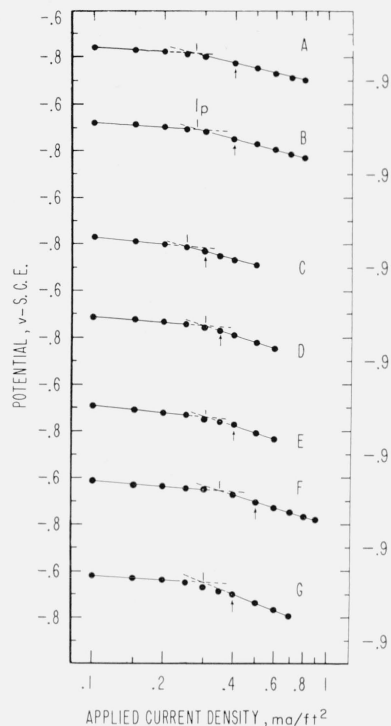


FIGURE 3. Cathodic polarization of an undisturbed inorganically coated steel specimen, No. 3, in a 3 percent sodium chloride solution for 29 days without cathodic protection.

Polarization rates, mv/ma, are as follows: A, 2100; B, 2400; C, 2670; D, 2570; E, 2600; F, 1960; G, 2500.

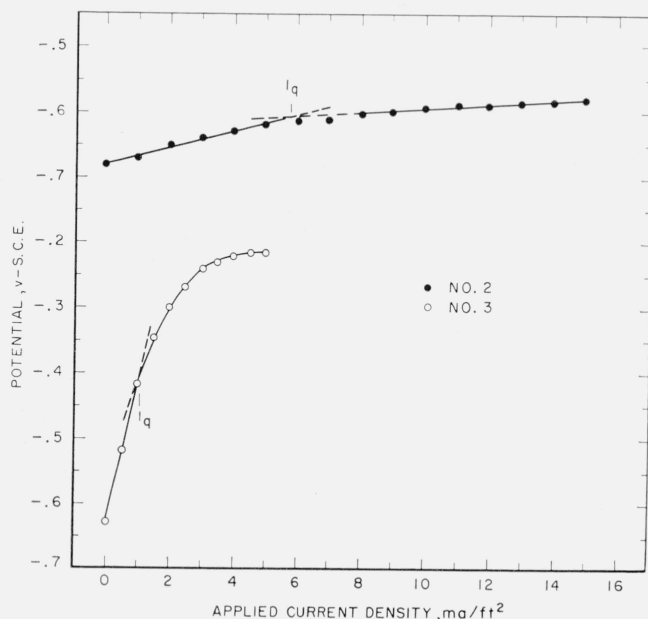


FIGURE 4. Anodic polarization of specimens Nos. 2 and 3 on the final day of exposure corresponding with the time when curves G (figs. 2 and 3) were obtained.

In order to compare the polarization of specimens No. 2 and 3 having inorganic coatings with that of the unprotected specimen, No. 1, the curves shown in figure 5 were obtained. Curves A and B were run while the specimen was covered with the thick accumulation of rust, curve A before removing the rod for exposure to the atmosphere for 12 days, curve B after the rod had been back in the salt water for 11 days following atmospheric exposure. Curves C through H were obtained on the same specimen during a 14-day exposure period after removing all the corrosion products and reexposing to the same solution. The specimen was weighed before and after the 14-day exposure period and anodic curves (fig. 6) were obtained to permit comparison of the calculated and actual weight losses during the period.

4. Interpretation of the Polarization Data

The purpose of the discussion which follows is to show how the applied currents associated with changes-in-slope in polarization curves (usually referred to as breaks) are related to the actual polarization over a specific range of the applied current (cathodic current here, because cathodic control predominated) and to show the relation between

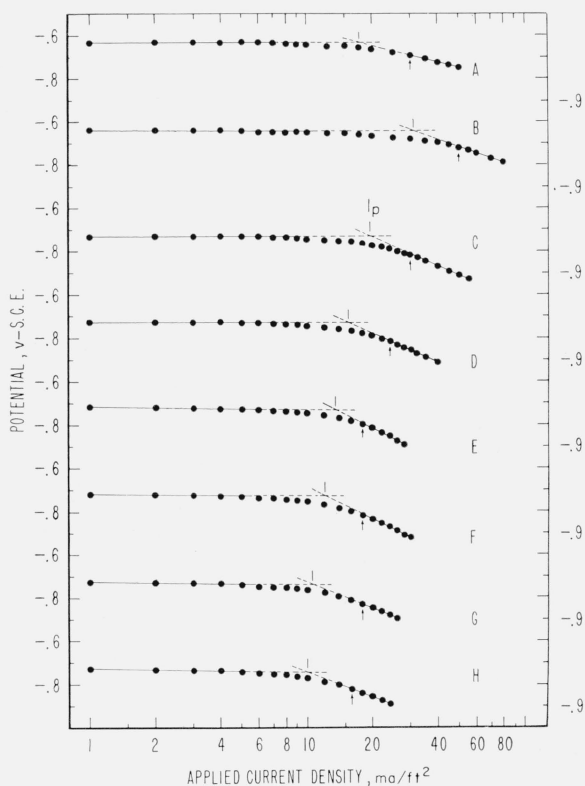


FIGURE 5. Cathodic polarization of a bare steel specimen, No. 1, in a 3 percent sodium chloride solution.

Curves A and B, after almost 4 years of exposure with 12 days of atmospheric exposure between polarization runs. Curves C through H, the same specimen after removing all corrosion products and exposing again to the same solution for 14 days. Polarization rates mv/ma are as follows: A, 21; B, 16; C, 29; D, 40; E, 47; F, 56; G, 58; H, 59.

these data and the rates of corrosion. Similar relationships, with some variation, were previously shown for steel corroding in soils [10]. The significance of the slopes of polarization curves in relation to rates of corrosion has since been discussed by others, namely, Simmons [11], Skold and Larson [12], and Stern [13].

Curves A and B, figure 5 were the only cathodic polarization curves obtained on specimen No. 1 (corroding freely) during the long exposure period, and while the specimen was covered with a thick adherent deposit of rust accumulated during almost 4 yrs of continuous exposure. Figure 7 shows the 3 specimens after 56 months of exposure to the salt water. The corrosion products on No. 1 are evident in the photograph. Reweighing of specimen No. 1 after the final cleaning revealed a weight loss of 11,835 mg during the intervening 1,356 days of exposure beginning after 12 months. Using the electrochemical equivalent ($K=2.8938 \times 10^{-4}$ g/coulomb) and assuming a corrosion efficiency of 100 percent, the average corrosion current density was calculated to be 3.5 ma/ft². It will be recalled that the average corrosion current density was 4.6 ma/ft² for the first 12 months. A dropping off of the corrosion rate with the passing of time is indicated. For this reason curves C through H, figure 5, and D through G, figure 6, were obtained to provide data on the corrosion rate of the clean steel rod during the first 14 days of exposure. The anodic curves, figure 6, are plotted on rectangular coordinate paper in order to permit a more accurate estimation of the current I_q , than was possible on logarithmic coordinates. The data shown in table 1 were obtained from figures 5 and 6 and are used to calculate [10] the weight loss over the 14-day period of exposure. The corrosion current decreased with time, being down to 6.8 ma/ft² after 10 days of exposure. The weight loss (299 mg) as calculated from the cathodic and anodic polarization curves compares reasonably well with the actual weight loss (280 mg).

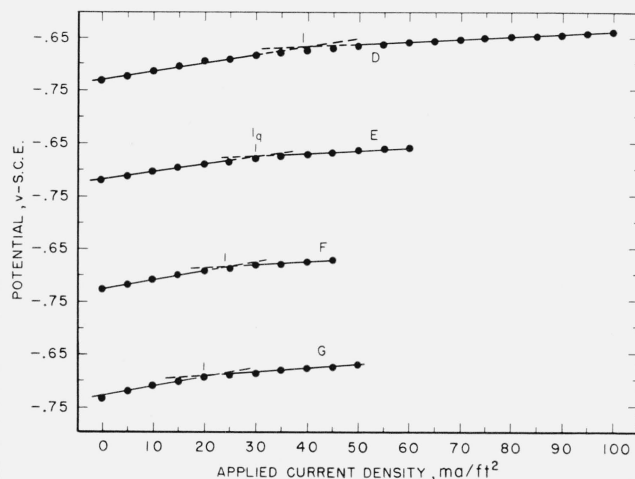


FIGURE 6. Anodic polarization of specimen No. 1 during the 14 day exposure period mentioned in figure 5.

Curves D, E, F, and G were obtained on the same day, respectively, as curves D, E, F, and G (fig. 5).

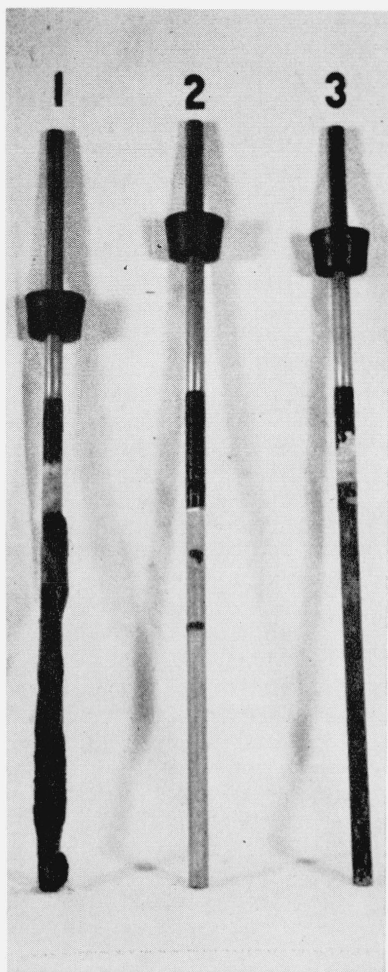


FIGURE 7. Appearance of steel specimens Nos. 1, 2, and 3 before final cleaning.

Rust spots account for most of the weight loss on specimen No. 2. The dark appearance below the tape on No. 3 is not rust but the color of the inorganic coating.

TABLE 1. Weight loss on specimen No. 1 caused by corrosion in 14 days

Calculations from polarization data (figs. 5 and 6)

Exposure time	Polarizing current ^a at break in curve		Corrosion ^b current i_o	Weight loss	
	Cathodic, I_p	Anodic, I_a		Calculated ^c cumulative	Actual
Days	ma	ma	ma	mg	mg
1	1.95 C	4.9 ^d	1.4	35	-----
2	1.55 E	3.9 D	1.1	66	-----
4	1.35 E	3.0 E	0.93	116	-----
7	1.20 F	2.4 F	.80	180	-----
10	1.05 G	2.0 G	.68	234	-----
14	1.00 H	1.9 ^e	.65	299	280

^a Measured values (density $\times 0.1$)—The capital letter following value of current designates the curve in fig. 5 or fig. 6 from which the value is obtained.

^b $i_o = I_p I_a / (I_p + I_a)$.

^c Weight loss (g) = Kti , where $K = 2.8938 \times 10^{-4}$ g per coulomb, $i = i_o$ —average current (amperes) for the period (t in seconds) between successive readings. For the period before the initial polarization run, the initial value of i_o was taken as average.

^d Based on the ratio I_a/I_p of the 2d day.

^e Based on the ratio I_a/I_p of the 10th day.

The high values of I_p (curves A and B, fig. 5) are not consistent with the corrosion rate, which presumably was at its lowest value when the data for these curves were obtained. Of course, there is no way of knowing what the corrosion current actually was at the time, except that it should be about equal to the average value (3.5 ma/ft²) previously calculated, based on the assumption that the corrosion rate was relatively stable for a long time. The answer does not lie in a change to anodic control, because an anodic polarization curve (not shown), obtained after curve B, showed that cathodic control predominated. It appears as though more work ought to be done to determine the effects of a heavy accumulation of corrosion products on polarization of the basis metal.

After 56 mo exposure and before finally completing the experiment it was decided, as previously mentioned, to leave specimen No. 2 without protective current, observe the effect of scratches in the coating on polarization and possibly measure the actual corrosion which had occurred. The polarization data for specimen No. 2 are shown in figures 2 and 4 and the corrosion calculations based on these data in table 2. The only other time in almost 5 yr of exposure that this specimen was subject to any corrosion was for a portion of the 3-day period after 42 mo of exposure. Based on subsequent measurements (table 2), the weight loss because of corrosion during this period was probably less than 5 mg. The weight loss calculations are based mainly on the cathodic polarization currents, I_p , as the anodic curve (fig. 4) showed that the control was cathodic. Use of the ratio $i_o = 0.73 I_p$ seems reasonable, in view of the data (table 1) obtained on specimen No. 1. Thus, for all practical purposes, in view of the agreement between actual and calculated weight losses, increases in I_p were indicative of increases in corrosion rate. This was reflected in curve D (fig. 2) as a result of a scratch in the coating purposely made on the preceding day. There was also some indication that exposure to the atmosphere for 12 days or the disturbance of the coating by a drop of dilute acid just prior to immersion increased the corrosion current (curve F).

The cathodic polarization curves (fig. 3) for specimen No. 3 cover three periods when there was no protective current. Although no corrosion was visible at any time during these periods, and no attempt was made to scratch the coating, the potentials at zero current (substantially the same as those shown for the lowest current on the abscissa) are electro-positive to the protective potential -0.77 v and hence it was assumed that the possibility of corrosion, however slight, did exist. This does not imply that the potentials per se gave proof of corrosion, but that the potentials (fig. 3) were in the same range as were the potentials of specimen No. 2 (fig. 2), when corrosion was known to be taking place. Thus, No. 3 was in the salt water for 29 days without protective current and for 21 days it is assumed, on the basis of the potential, that some corrosion could have occurred. During the almost 5 yr that this specimen was under cathodic protection, there was only one

TABLE 2. Weight loss on specimen No. 2 resulting from corrosion due to scratches in the coating

Corrosion is calculated from the polarization data (figs. 2 and 4).

Exposure time	Polarizing current ^a at break in curve		Corrosion ^b current i_o	Weight loss	
	Cathodic I_p	Anodic I_q		Calculated ^c cumulative	Actual
Days	ma	ma	ma	mg	mg
1	0.072A	-----	0.053	1.3	-----
2	.084B	-----	.061	2.7	-----
5	.098C	-----	.071	7.6	-----
6	.17D	-----	.12	10.0	-----
12	.16E	-----	.12	28.00	-----
14	(d)	-----	-----	34.0	-----

The specimen was removed from the salt water on the 14th day and put back in again on the 26th day. Corrosion during this interim (12 days) was considered as negligible.

27	.19F	-----	.14	37.5	-----
37	.20G	0.55 ^e	.15	75.0	70

^a Measured values (density $\times 0.1$). The capital letter following a value of current designates the curve (fig. 2) from which the value is obtained.

^b $i_o = I_p I_q / (I_p + I_q)$, based on I_q/I_p ratio for the 37th day or $i_o = 0.73 I_p$.

^c Same as footnote ^c, table 1.

^d Used 0.16 ma for I_p .

^e From fig. 4.

occasion, over a weekend, when the current accidentally went off, as described in the previous section. The only anodic polarization curve on specimen No. 3 was obtained on the last day of exposure and is shown in figure 4. Based on this curve and curve G (fig. 3), the ratio I_q/I_p = approx. 3, and therefore, $i_o = 0.75 I_p$. Using the value $I_p = 0.03$ ma (specimen area = 0.1 ft²) from figure 3 as the average value for 21 days and calculating as previously, the calculated weight loss was about 12 mg. The actual weight loss during the 5 yr was 35 mg. The only visual evidence of corrosion on the cleaned specimen was on the lower-half of the taped area and also above the tape, where salt had crystallized and penetrated the oil film. As the calculated corrosion would not include the area above the tape which was out of the solution, the calculated value seems to be quite reasonable.

It is known from experience that there are times when it is difficult to observe significant breaks in polarization curves. The relative importance of cathodic and anodic polarization curves in estimating rates of corrosion was discussed several years ago [10]. It was observed that, for steel in soils, a relation existed between the rate of polarization ($\Delta V/\Delta I$ resulting from externally applied current) and the applied current I_p (at the break in curve). It was also shown that both of these factors were related to the instantaneous rates of corrosion. The most useful values of ΔV seemed to be those potential changes which occurred in a range of applied currents of the order of I_p or slightly larger.

Simmons [11] found that inhibitors could be evaluated by $\Delta E/\Delta I$ (called $\Delta V/\Delta I$ in this paper) from polarization curves. Small current densities caused changes in potential on exposed steel of 100 mv and more. In figures 2 and 3 of Simmon's paper are shown cathodic curves for steel in salt water with and without the inhibitor Na₂CrO₄. We noted that in both of Simmon's figures the changes in potential of the d-c null curves, from the lowest currents to

the values at the breaks (corresponding to our I_p values), are about equal. As these currents were of the relative magnitude of 10 to 1, Simmon's conceded this to be the relative magnitude of the corrosion currents which were either comparable in magnitude or less than the currents at the breaks in his curves. Thus, the ratios $\Delta E/\Delta I$ for these data were in the reverse order, namely 1 to 10.

Skold and Larson [12] showed that an empirical relation existed between the slopes ($\Delta E/\Delta I$) of polarization curves for low values of applied current and the corrosion rates of steel in fresh water as determined by weight losses. They first tried correlating the breaks in polarization curves with corrosion rates but abandoned this in favor of the slope method. It is believed that the use of a null circuit is necessary for the detection of breaks in polarization curves obtained with a 3000 ohm-cm solution such as was used by Skold and Larson. Nevertheless, their straight line relationship on logarithmic coordinates between corrosion rate and $\Delta E/\Delta I$ seems to have considerable merit. This has been further substantiated by the data reported in this paper.

Stern [13] has published the theoretical basis for the method of Skold and Larson. He has stressed the importance of applying polarizing currents which are smaller than the presumed corrosion currents in order to avoid marked polarization with resultant possible changes in the inherent rates of corrosion. Apparently, the inherent rates of corrosion observed in the present study were unaffected by the applied currents which at the end of a run were often 4 times the magnitude of the corrosion currents. This is also true of previous studies [7, 9] where controls subjected to reasonable amounts of polarization lost no more weight than those on which no polarization runs were made. Possibly the short polarizing time (10 to 15 min) is beneficial in negating this tendency.

The polarization data (figs. 2 to 6 incl.) were plotted from the strip chart records for additional interpretation and condensation. Furthermore, on the logarithmic current scale, the straight line portion of the cathodic curve, for applied currents larger than I_p , becomes helpful in estimating $\Delta V/\Delta I$. The values of $\Delta V/\Delta I$ shown in figures 2, 3, and 5 were calculated from changes in potential between zero applied current and the currents indicated by the arrows (beginning of straight line) where all local action corrosion is presumed to have ceased. Figure 8 shows the relation between $\Delta V/\Delta I$ and corresponding values of I_p for the 3 specimens. It is interesting to note that the plot of these parameters on the logarithmic coordinates results in a slope close to the theoretical value of minus one mentioned by Stern [13], although he considered corrosion current instead of the current I_p . Thus, figure 8 suggests, at least for steel in aqueous solutions, that a fairly constant ratio exists between the corrosion current and the current I_p . The calculations of weight loss in tables 1 and 2 are to some extent based on this premise. The small variations in the ratio i_o/I_p may be attributed to errors in selecting the break current I_q ,

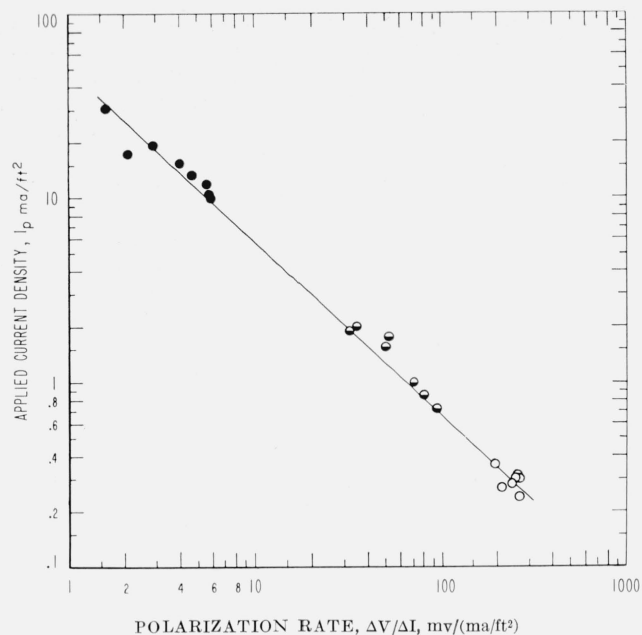


FIGURE 8. Relationship during cathodic polarization of steel specimens Nos. 1, 2, and 3 between the current, I_p , at the break and the polarization rate, $\Delta V/\Delta I$, on logarithmic coordinates.

●, Specimen No. 1 (fig. 5); ◐, No. 2 (fig. 2); ○, No. 3 (fig. 3).

from the anodic polarization curves. The selection of I_q is more subject to error than I_p when the corrosion reaction is under cathodic control. It is fortunate though that the accuracy with which the corrosion current can be calculated depends chiefly on the more significant curve which also lends itself to the better interpretation. In a case of corrosion under anodic control, this would be the anodic curve.

In order to further compare the data (fig. 8) with that of Skold and Larson, the actual weight losses of specimens 1 and 2 (tables 1 and 2) and the calculated weight loss of specimen 3 were related to the polarization rates $\Delta V/\Delta I$ in their units of measurement (fig. 9). The NBS weight losses, even though for only 3 specimens, carry considerable significance because of their range. The values are time-averaged and cover time periods of 14, 25, and 21 days, respectively, for specimens Nos. 1, 2, and 3. The calculated weight loss was used for No. 3 because, as previously stated, the actual value (35 mg) consisted chiefly of corrosion loss which occurred outside of the electrolyte and therefor could not be accounted for by the polarization measurements. Curves B and C were drawn from the data (fig. 1) of Skold and Larson [12]. Curve B covers approximately their range of data in the 3000 ohm-cm water and curve C is based on the mean value of each of two groups of their data. Curves B and C are subject to some resistance error, B more than C, as mentioned by Skold and Larson and also by Stern [13] and therefore have greater negative slopes than has the NBS curve, A.

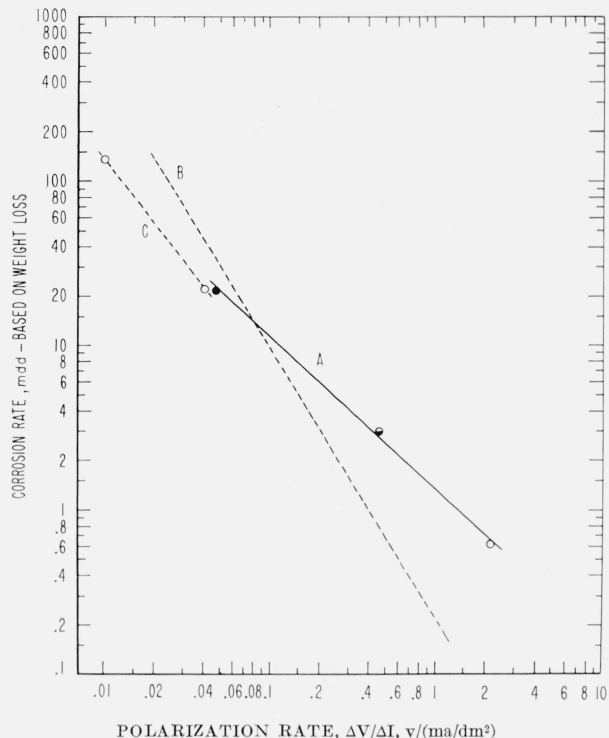


FIGURE 9. Logarithmic relationship between actual corrosion (weight loss) and cathodic polarization rate of steel.

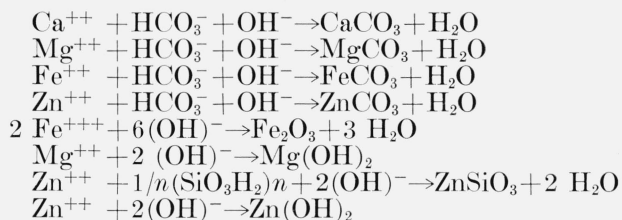
Curve A (NBS), ● Specimen No. 1, ◐ No. 2, ○ No. 3 all in about 35 ohm-cm solution. Curves B and C [Skold and Larson] in 3000 ohm-cm water and 350-850 ohm-cm solution, respectively.

5. Nature of the Coatings

After 57 months of exposure, approximately 50 mg of coating was taken from specimens Nos. 2 and 3 for analysis. The results of the spectrochemical analyses are shown in table 3. The coating of specimen No. 2 consisted mainly of carbonates (27% CO_3) and silicates associated with calcium, magnesium, iron, and zinc. As the coating was almost white in appearance, the iron content was probably at the lower limit of the indicated range. The coating on specimen No. 3 was primarily in the form of carbonates (56% CO_3) combined with decreasing amounts of calcium, magnesium, and iron, in that order. Some silicate was also present. The zinc and silicates apparently constitute the chief differences in coating composition of the two specimens. The coating of specimen No. 2 had both of these elements in considerable proportion, whereas, the coating on specimen No. 3 did not, it being chiefly calcium carbonate with minor amounts of magnesium carbonate and iron oxide. It was estimated that during the 57 months about 300 liters of city water, which accounted for the formation of the coatings, were poured into each specimen jar to replace the water lost by evaporation. A composite mineral analysis of the city water (District of Columbia) for the year 1958 (avg) is shown in table 4.

The saline solution surrounding specimen No. 2 probably had a zinc ion concentration corresponding to the solubility product of zinc carbonate or hydroxide. Carbonates were evident as a sediment in the container. A sediment of carbonates was also very noticeable in the jar containing specimen No. 3.

The alkaline reactions that occur on the surface of steel during cathodic protection result in precipitates which either adhere to the metal surface as a coating or drop as a sediment. Some of the possible reactions are:



As a result of the foregoing reactions, the compounds formed can recombine and form other molecular compounds. The proportion of any one compound in the composition of the precipitate depends upon its solubility and the constituents of the solution. Based on table 3, the coating on specimen No. 2 was, in addition to calcium carbonate, probably zinc silicate. It is believed that the large amount of silicates in the coating of specimen No. 2 can be attributed to the zinc in solution from the anode. This conclusion is reinforced by the general knowledge that zinc is effective in precipitating silicates out of solution. The relative absence of silicates in the coating on specimen No. 3 can only be attributed to the relative absence of zinc, as the solutions were similar, but a carbon rather than zinc anode was used for cathodic protection.

TABLE 3. Results of spectrochemical analyses of coatings formed on specimens nos. 2 and 3

Element	Specimen		Element	Specimen	
	No. 2	No. 3		No. 2	No. 3
Ag	VW	T	Li	T	T
Al	M	W	Mg	S	S
B	T	-----	Mn	M	W
Ba	W	W	Na	M	M
Ca	VS	VS	Ni	W	VW
Cd	W	-----	Pb	M	W
Co	VW	-----	Pt	VW	-----
Cr	W	VW	Si	VS	-----
Cu	M	W	Sr	M	M
Fe	S	S	Ti	VW	W
K	VW	VW	Zn	S	-----

NOTE: In general, VS means greater than 10%; S, 1 to 10%; M, 0.1 to 1.0%; W, 0.01 to 0.1%; VW, 0.001 to 0.01%; T, 0.0001 to 0.001%; -----, not detected.

The mechanism of electrophoresis may be a contributing factor in the formation of the coatings. Such a hypothesis would necessarily involve the attraction of positively-charged colloidal particles to the cathode. Although a highly conductive solution, such as 3 percent NaCl, is not a favorable environment for electrophoresis to take place, it is believed that over a long period of time the contribution of the mechanism to the formation of the coating, although perhaps taking place slowly, might be a significant factor. Thus, the formation of coatings on specimens Nos. 2 and 3 may then be attributed to two factors, first, the precipitation of relatively insoluble compounds, such as carbonates, silicates, and others in physical contact with the specimen surfaces and, second, the electrophoretic deposition of colloidal particles in the pores of the coating.

A cathodically protected surface promotes conditions favorable for the precipitation of carbonates, phosphates, hydroxides, and silicates. If the protective current is excessive as the coating forms, the alkalinity around the uncoated areas will promote additional precipitation farther from the cathode surface because of the diffusion of hydroxide away from the cathode. On the other hand, a reduction of the protective current, consistent with the protective potential requirement, would tend to lessen this diffusion. For the formation of a compact coating, the volume and mass of insoluble colloidal particles might also be considered. It is believed that both volume and mass of the colloids increase with time during the precipitation process. Excessive alkalinity around the cathode areas, for example as a result of too much current, will promote this increase because the precipitation begins further away from the cathodic areas. This will result in two unfavorable effects, first, a slowing down of the migration of colloids toward the cathode and, second, the inability of the larger colloids which do arrive at the cathode to fill in the pores of the coating already in the formative stage. On the other hand, lower alkalinity in the porous or uncoated areas, as a result of reduced current, will result in smaller colloidal particles arriving at the surface, better penetration of the pores and hence a more compact coating. This condition is approached by reducing the protective current to the optimum value (consistent with protective potential) for cathodic protection.

The foregoing discussion might be evaluated by considering the properties of the inorganic coatings which were actually formed on specimens Nos. 2 and 3. During the first 24 months of exposure, the coating on No. 2 apparently was superior to that on No. 3, as evidenced by the heavier coating on the former.

TABLE 4. Mineral analysis of District of Columbia water supply—mg/liter

Total solids	Loss ign.	SiO ₂	Ca	Cl	CO ₂	F ⁻	Fe	HCO ₃	Mg	Mn	NO ₂	NO ₃	SO ₄	Alk. CaCO ₃	Tot. hard CaCO ₃	N.C.H. CaCO ₃
157	37	5.9	31.7	10.0	2.1	1.00	.026	78	6.5	0	0	0.73	37.3	64	106	42

It was also observed that the protective current density on No. 3 was several times greater than on No. 2. Current densities were about the same the following year and after 24 months the weight of coating formed on No. 2 was at least 4 times that on No. 3 (25 mg). However, during the period between the 33d and 57th month of exposure the protective current to specimen No. 3 was progressively lowered by reducing the applied voltage to that value which brought the potential of the specimen to -0.77 v. Eventually the current to No. 3 was smaller than that to No. 2, and the polarization of No. 3 was accomplished at a smaller current density than the polarization of No. 2 (fig. 8).

When the specimens were being cleaned for final reweighing, the coating on No. 3 was observed to be considerably more adherent than that formed on No. 2, even after subjecting the specimens to cathodic cleaning (1 amp/ft^2) for 2 hr. The coating on No. 2 was scraped off rather easily with a brass scraper but that formed on No. 3 had to first be hammered loose by tapping. Unfortunately, no accurate comparison of coating weights can be given, but based on the weight of a portion (500 mg) of the coating removed from No. 3, it was conservatively estimated that the coating formed on No. 3 weighed about 1000 mg and its thickness was about 0.010 in. Thus, the thickness, adherence, and protective value of the coating apparently increased after lowering the protective current to the optimum value as determined by the potential of the specimen.

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